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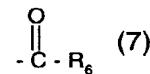
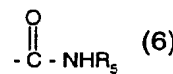
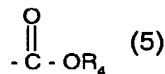
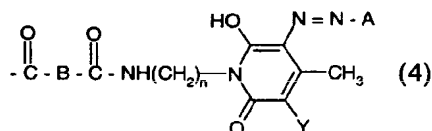
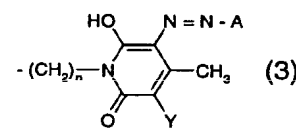
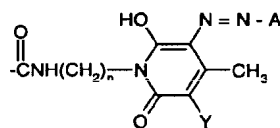
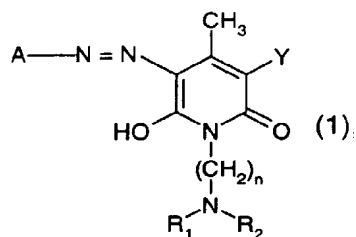
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(54) Title: PYRIDONE DYES, A PROCESS FOR THEIR PREPARATION AND THEIR USE IN THE PRODUCTION OF COLOURED PLASTICS OR POLYMERIC COLOUR PARTICLES



(57) **Abstract:** The present invention relates to pyrifone azo dyes of formula (1), wherein A is the radical of a diazo component of the benzene, naphthalene, diphenyl, azobenzene, thiophene, benzothiazole, benzoisothiazole, thiadiazole, indazole, benzotriazole, pyrazole, anthraquinone, naphththolic acid imide, chromone, phthalimide or diphenylene oxide series, R₁ is hydrogen, unsubstituted or hydroxyl- or phenyl- substituted C₁-C₆alkyl, it being possible for the alkyl chain to be interrupted from C₃ upwards by one or more oxygen atoms, or has the meanings of R₂, R₂ is a radical of formulae (2), (3), (4), (5), (6), or (7), wherein B is a bridging member, R₄ is alkyl or aryl, R₅ and R₆ are each independently of the other alkyl, aryl or heteroaryl and A is as defined for formula (1), or R₁ and R₂ together with the nitrogen atom in NR₁R₂ form a heterocyclic ring, Y is cyano, -CONH₂ or CH₂SO₃H, and n is an integer from 2 to 6, to a process for their preparation and to their use in the production coloured plastics or polymeric colour particles.



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Pyridone dyes, a process for their preparation and their use in the production of coloured plastics or polymeric colour particles

The present invention relates to pyridone azo dyes, to their preparation and to their use in the production of coloured plastics or polymeric colour particles.

Pyridone azo dyes and their use in dyeing semi-synthetic or synthetic hydrophobic fibre materials are known. When the known pyridone azo dyes are used for mass-colouring synthetic materials (plastics), it has been shown, however, that those dyes do not always fully satisfy the highest demands, especially in respect of heat resistance, migratability and/or tinctorial strength. There is therefore a need for new pyridone azo dyes that yield thermostable tinctorially strong mass-colorations and exhibit good allround fastness properties.

It has now been found, surprisingly, that the pyridone azo dyes according to the invention meet the criteria given above to a considerable degree.

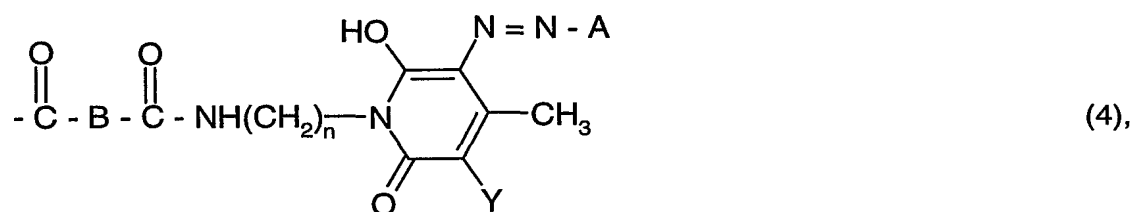
The present invention accordingly relates to pyridone azo dyes of formula



wherein

A is the radical of a diazo component of the benzene, naphthalene, diphenyl, azobenzene, thiophene, benzothiazole, benzisothiazole, thiadiazole, indazole, benzotriazole, pyrazole, anthraquinone, naphtholic acid imide, chromone, phthalimide or diphenylene oxide series, R₁ is hydrogen, unsubstituted or hydroxy- or phenyl-substituted C₁-C₆alkyl, it being possible for the alkyl chain to be interrupted from C₃ upwards by one or more oxygen atoms, or has the meanings of R₂, R₂ is a radical of formula

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wherein B is a bridging member, R₄ is alkyl or aryl, R₅ and R₆ are each independently of the other alkyl, aryl or heteroaryl and A is as defined for formula (1), or

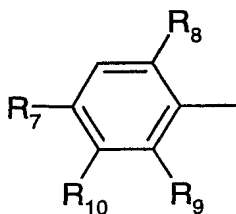
R₁ and R₂ together with the nitrogen atom in -NR₁R₂ form a heterocyclic ring,

Y is cyano, -CONH₂ or -CH₂SO₃H, and

n is an integer from 2 to 6.

A is preferably the radical of a diazo component of the benzene series.

Especially preferable as A is a radical of formula



(8),

wherein

R₇ is hydrogen or halogen,

R₈ is hydrogen, halogen, cyano, -CF₃, -COOR₁₁ wherein R₁₁ is C₁-C₄alkyl and the alkyl chain can be interrupted by oxygen, or is benzyl or -SO₂R₁₂ wherein R₁₂ is -NR₁₃R₁₄ or phenyl and R₁₃ is hydrogen or C₁-C₄alkyl and R₁₄ is C₁-C₄alkyl or benzyl,

R₉ is hydrogen or halogen, and

R₁₀ is hydrogen or a radical -SO₂-O-C₆H₅.

C₁-C₆Alkyl as R₁ is, for example, methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, amyl, tert-amyl (1,1-dimethylpropyl), 1,1,3,3-tetramethylbutyl, hexyl, 1-methylpentyl, neopentyl, cyclopentyl, cyclohexyl, and the associated isomers and especially methyl. R₁ is preferably methyl, ethyl or the radical -CO-R₆ (7) and especially hydrogen.

Alkyl in the definition of R₄, R₅ and R₆ is, for example, C₁-C₄alkyl, such as methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, sec-butyl and tert-butyl, and also C₁-C₄alkyl substituted by C₁-C₂alkoxy or by benzyloxy, or C₅-C₆cycloalkyl, such as cyclopentyl and cyclohexyl.

Aryl in the definition of R₄, R₅ and R₆ is, for example, phenyl or naphthyl.

A heterocyclic ring formed by R₁, R₂ and the nitrogen atom in -NR₁R₂ is, for example, a heterocyclic ring of the phthalimidyl, lactam or saccharin series.

Heteroaryl in the definition of R₅ is, for example, thiazolyl, triazolyl or thiadiazolyl.

Heteroaryl in the definition of R₆ is, for example, thiophene or furan.

C₁-C₄Alkyl as R₁₁, R₁₃ and R₁₄ is methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, sec-butyl or tert-butyl.

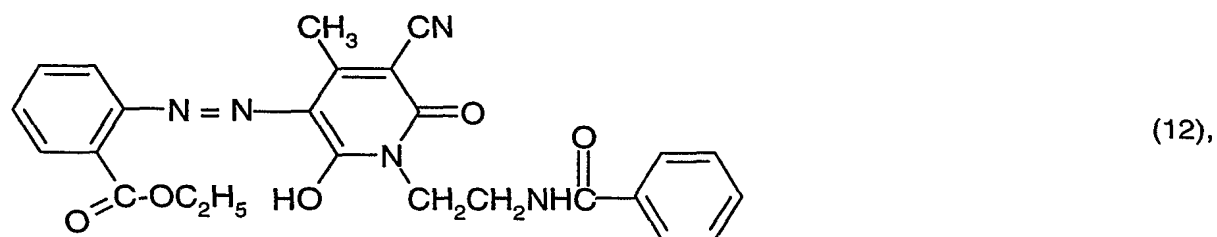
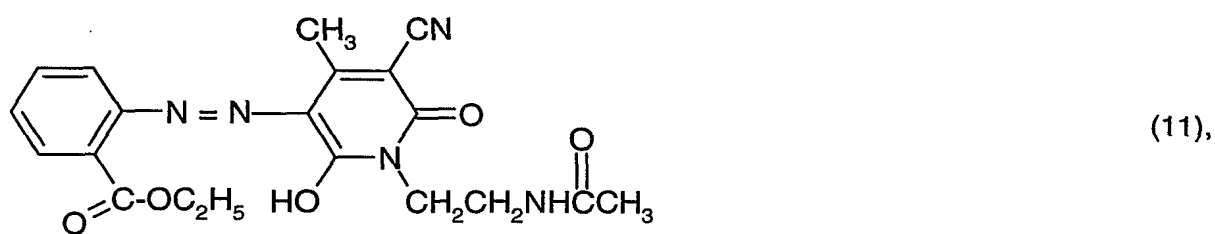
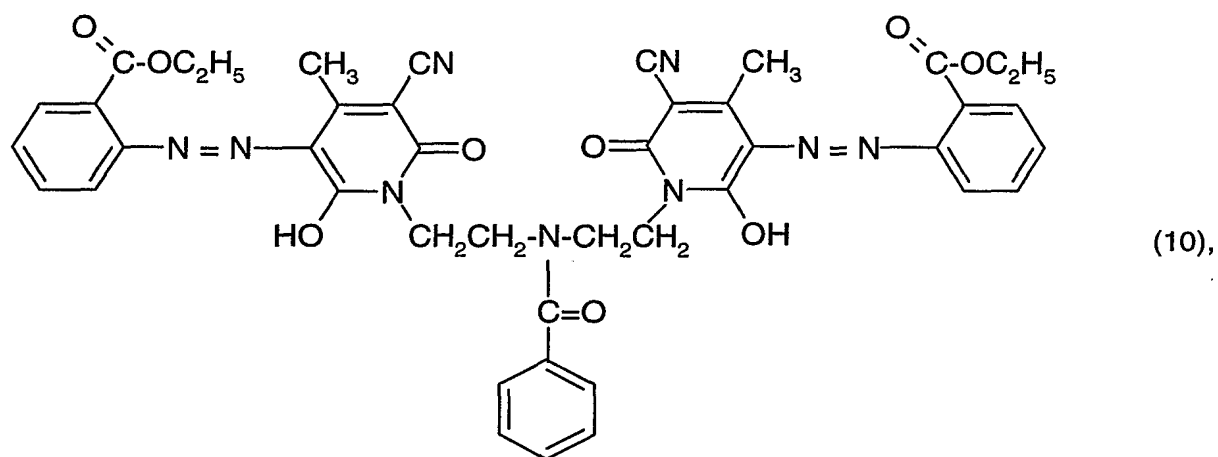
Y is preferably cyano.

Halogen as R₇, R₈ and R₉ is bromine, iodine and especially chlorine.

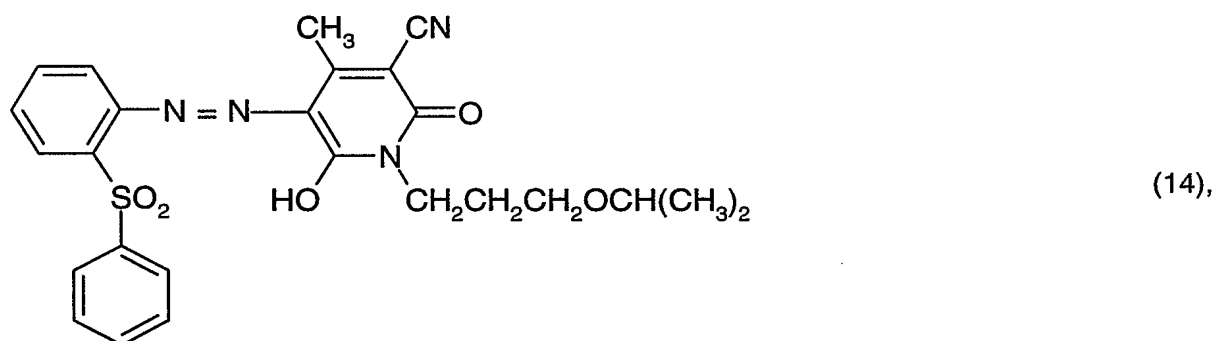
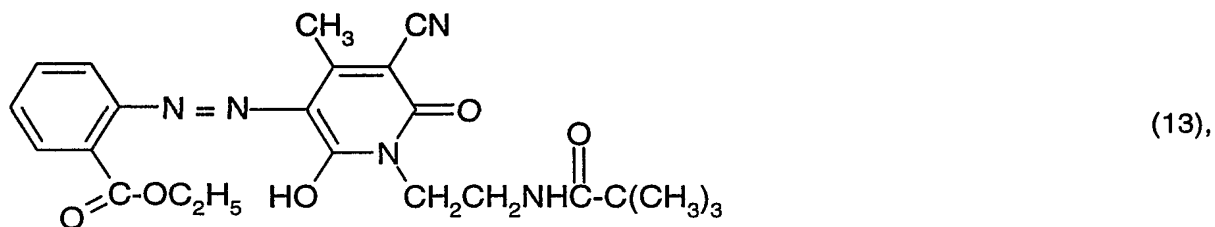
The bridging member B is, for example, phenylene, naphthylene, thienyl or furyl.

n is preferably a number from 2 to 4, especially 2 or 3.

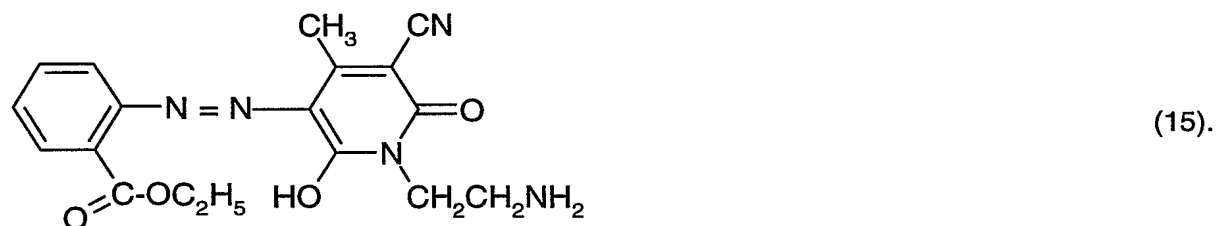
Special preference is given to pyridone azo dyes of formulae



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and

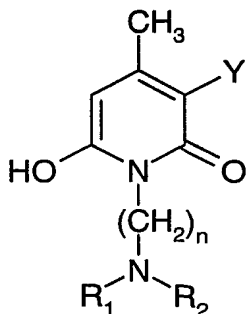


The present invention relates also to a process for the preparation of the pyridone azo dyes of formula (1) according to the invention.

The dyes are prepared, for example, as follows: a compound of formula

A - NH₂ (50)

is diazotised in accordance with a customary procedure and then coupled to a coupling component of formula



(51),

A, R₁, R₂, Y and n being as defined above for formula (1).

The diazotisation of the compound of formula (50) is carried out in a manner known *per se*, for example with sodium nitrite in an acidic, e.g. hydrochloric-acid-containing or sulfuric-acid-containing, aqueous medium. The diazotisation may, however, also be carried out using other diazotisation agents, e.g. using nitrosylsulfuric acid. In the diazotisation, an additional acid may be present in the reaction medium, e.g. phosphoric acid, sulfuric acid, acetic acid, propionic acid, hydrochloric acid or a mixture of such acids, e.g. a mixture of propionic acid and acetic acid. The diazotisation is advantageously carried out at temperatures of from -10 to 30°C, for example from -10°C to room temperature.

The coupling of the diazotised compound of formula (50) to the coupling component of formula (51) is likewise effected in known manner, for example in an acidic, aqueous or aqueous-organic, medium, advantageously at temperatures of from -10 to 30°C, especially below 10°C. Examples of acids used are hydrochloric acid, acetic acid, propionic acid, sulfuric acid or phosphoric acid.

The compounds of formula (50) are known or can be prepared in a manner known *per se*.

The coupling components of formula (51) are known or can be prepared in a manner known *per se*, for example by reacting a compound of formula



first with a compound of formula

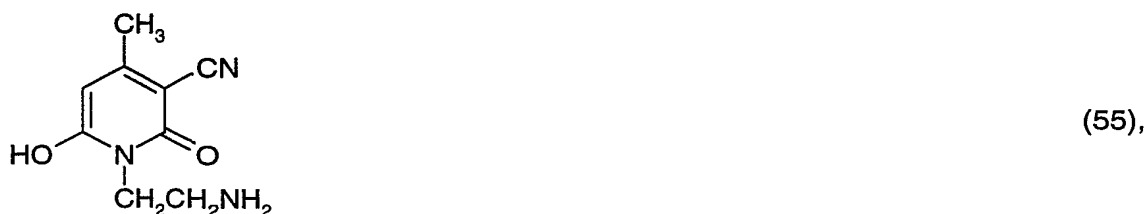


and then with a compound of formula

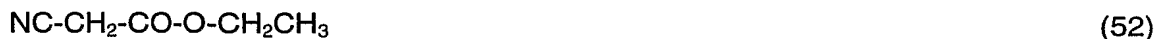


to form a compound of formula

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or, for example, by reacting 2 mol of a compound of formula



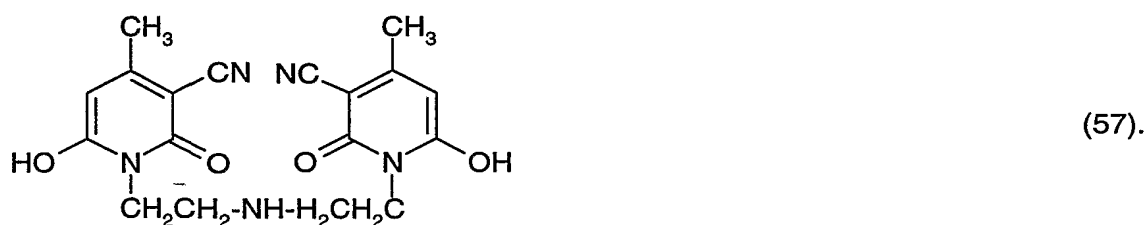
first with a compound of formula



and then with 2 mol of a compound of formula



to form a compound of formula



Starting from the compounds of formulae (55) and (57), the corresponding compounds of formula (51) can then be prepared in a manner known *per se* by the further reaction of the amino group, for example with benzoyl chloride or acetyl chloride.

The compounds of formulae (52) to (54) and (56) are known and can be prepared in a manner known *per se*.

The present invention relates also to a process for the production of coloured plastics or polymeric colour particles, which comprises mixing together a high molecular weight organic material and a tinctorially effective amount of at least one pyridone azo dye of formula (1).

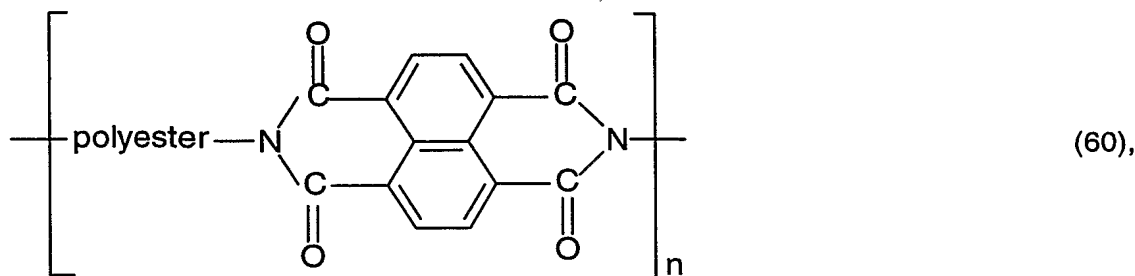
The colouring of high molecular weight organic substances with the pyridone azo dye of formula (1) is carried out, for example, by mixing such a pyridone azo dye into those substrates using roll mills, mixing apparatus or grinding apparatus, with the result that the pyridone azo dye is dissolved or finely dispersed in the high molecular weight material. The high molecular weight organic material with the admixed pyridone azo dye is then processed using processes known *per se*, for example calendering, compression moulding, extrusion,

coating, spinning, casting or injection moulding, whereby the coloured material acquires its final form. It is also possible for the admixing of the pyridone azo dye to be carried out immediately prior to the actual processing step, for example by continuously feeding a pulverulent pyridone azo dye and, at the same time, a granulated or pulverulent high molecular weight organic material, and optionally also additional ingredients, e.g. additives, directly into the intake zone of an extruder, where mixing takes place just before processing. In general, however, it is preferable for the pyridone azo dye to be mixed into the high molecular weight organic material beforehand, because more even coloration of the substrates can be obtained.

It is often desirable, in order to produce non-rigid mouldings or to reduce their brittleness, to incorporate so-called plasticisers into the high molecular weight compounds prior to shaping. There may be used as plasticisers, for example, esters of phosphoric acid, phthalic acid or sebacic acid. In the process according to the invention the plasticisers may be incorporated into the polymers before or after the incorporation of the colorant. It is also possible, in order to achieve different shades of colour, to add to the high molecular weight organic materials, in addition to the pyridone azo dye of formula (1), also further pyridone azo dyes or other colorants in any desired amounts, optionally together with further additives, e.g. fillers or siccatives.

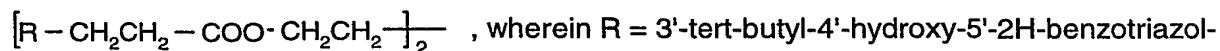
In order to improve the light fastness properties, UV absorbers are advantageously mixed into the plastics or polymeric particles to be coloured with the pyridone azo dye of formula (1) according to the invention. The amount of UV absorber can vary within a wide range; advantageously there is used from 0.01 to 1.0 % by weight, especially from 0.05 to 0.6 % by weight, more especially from 0.1 to 0.4 % by weight, of a UV absorber, based on the weight of the plastics or polymeric particles.

Suitable UV absorbers are especially 2-(2'-hydroxyphenyl)benzotriazoles, 2-hydroxybenzophenones, esters of substituted or unsubstituted benzoic acid, acrylates, oxamides, 2-(2-hydroxyphenyl)-1,3,5-triazines, monobenzoates of resorcinol or formamidines, and a polyester UV absorber of formula



having a specific weight of from 1200 to 1400, preferably from 1300 to 1350, at 25°C.

From the class of the 2-(2'-hydroxyphenyl)benzotriazoles there may be mentioned, for example, 2-(2'-hydroxy-5'-methylphenyl)benzotriazole, 2-(3',5'-di-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(5'-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(2'-hydroxy-5'-(1,1,3,3-tetramethylbutyl)phenyl)benzotriazole, 2-(3',5'-di-tert-butyl-2'-hydroxyphenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-methylphenyl)-5-chlorobenzotriazole, 2-(3'-sec-butyl-5'-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(2'-hydroxy-4'-octyloxyphenyl)benzotriazole, 2-(3',5'-di-tert-amyl-2'-hydroxyphenyl)benzotriazole, 2-(3',5'-bis(α,α-dimethylbenzyl)-2'-hydroxyphenyl)benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-octyloxy-carbonyl-ethyl)phenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-5'-[2-(2-ethylhexyloxy)carbonyl-ethyl]-2'-hydroxyphenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-methoxycarbonyl-ethyl)phenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-methoxycarbonyl-ethyl)phenyl)benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-octyloxy-carbonyl-ethyl)phenyl)benzotriazole, 2-(3'-tert-butyl-5'-[2-(2-ethylhexyloxy)carbonyl-ethyl]-2'-hydroxyphenyl)benzotriazole, 2-(3'-dodecyl-2'-hydroxy-5'-methylphenyl)benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-iso-octyloxy-carbonyl-ethyl)phenyl)benzotriazole, 2,2'-methylene-bis[4-(1,1,3,3-tetramethylbutyl)-6-benzotriazol-2-ylphenol]; the transesterification product of 2-[3'-tert-butyl-5'-(2-methoxycarbonyl-ethyl)-2'-hydroxyphenyl]-2H-benzotriazole with polyethylene glycol 300;



2-ylphenyl; 2-[2'-hydroxy-3'-(α,α-dimethylbenzyl)-5'-(1,1,3,3-tetramethylbutyl)phenyl]-benzotriazole; and 2-[2'-hydroxy-3'-(1,1,3,3-tetramethylbutyl)-5'-(α,α-dimethylbenzyl)phenyl]-benzotriazole.

From the class of the 2-hydroxybenzophenones there may be mentioned, for example, the 4-hydroxy, 4-methoxy, 4-octyloxy, 4-decyloxy, 4-dodecyloxy, 4-benzyloxy, 4,2',4'-trihydroxy and

2'-hydroxy-4,4'-dimethoxy derivatives.

From the class of the 2-(2-hydroxyphenyl)-1,3,5-triazines there may be mentioned, for example, 2,4,6-tris(2-hydroxy-4-octyloxyphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2,4-dihydroxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2,4-bis(2-hydroxy-4-propyloxyphenyl)-6-(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(4-methylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-dodecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-tridecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-butyloxypropyloxy)phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-octyloxypropyloxy)phenyl]-4,6-bis(2,4-dimethyl)-1,3,5-triazine, 2-[4-(dodecyloxy/tridecyloxy-2-hydroxypropoxy)-2-hydroxyphenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-dodecyloxypropoxy)phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-hexyloxy)phenyl-4,6-diphenyl-1,3,5-triazine, 2-(2-hydroxy-4-methoxyphenyl)-4,6-diphenyl-1,3,5-triazine, 2,4,6-tris[2-hydroxy-4-(3-butoxy-2-hydroxypropoxy)phenyl]-1,3,5-triazine and 2-(2-hydroxyphenyl)-4-(4-methoxyphenyl)-6-phenyl-1,3,5-triazine.

From the class of the oxamides there may be mentioned, for example, 4,4'-dioctyloxyoxanilide, 2,2'-diethoxyoxanilide, 2,2'-dioctyloxy-5,5'-di-tert-butoxanilide, 2,2'-didodecyloxy-5,5'-di-tert-butoxanilide, 2-ethoxy-2'-ethyloxanilide, N,N'-bis(3-dimethylaminopropyl)oxamide, 2-ethoxy-5-tert-butyl-2'-ethyloxanilide and a mixture thereof with 2-ethoxy-2'-ethyl-5,4'-di-tert-butoxanilide and mixtures of o- and p-methoxy-disubstituted oxanilides and mixtures of o- and p-ethoxy-disubstituted oxanilides.

As esters of substituted or unsubstituted benzoic acid there may be mentioned, for example, 4-tert-butylphenyl salicylate, phenyl salicylates, octylphenyl salicylates, dibenzoylresorcinol, bis(4-tert-butylbenzoyl)resorcinol, benzoylresorcinol, 2,4-di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxybenzoate, hexadecyl 3,5-di-tert-butyl-4-hydroxybenzoate, octadecyl 3,5-di-tert-butyl-4-hydroxybenzoate or 2-methyl-4,6-di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxybenzoate.

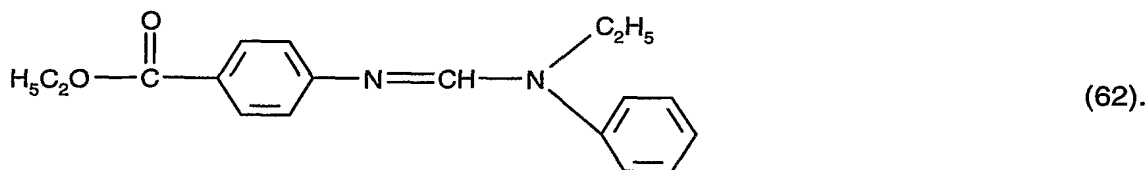
From the class of the acrylates there may be mentioned, for example, ethyl- α -cyano- β,β -diphenylacrylate, isooctyl- α -cyano- β,β -diphenylacrylate, methyl- α -carbomethoxycinnamate, methyl- α -cyano- β -methyl-p-methoxycinnamate, butyl- α -cyano- β -methyl-p-methoxy-

cinnamate, methyl- α -carbomethoxy-p-methoxycinnamate or N-(β -carbomethoxy- β -cyanovinyl)-2-methylindoline.

A resorcinol monobenzoate is, for example, a compound of formula



A formamidine is, for example, a compound of formula



Preference is given to the colouring of thermoplastic plastics, especially in the form of fibres, granules or mouldings, for example containers for solid or liquid substances, for example bottles. Preferred high molecular weight organic materials to be coloured according to the invention are very generally polymers having a dielectric constant of ≥ 2.5 , especially polyester, polycarbonate (PC), polystyrene (PS), polymethyl methacrylate (PMMA), polyamide, polyethylene, polypropylene, styrene/acrylonitrile (SAN) or acrylonitrile/butadiene/styrene (ABS). Polyester and polyamide are especially preferred. Very special preference is given to linear aromatic polyesters obtainable by polycondensation of terephthalic acid or naphthalene-2,6-dicarboxylic acid and glycols, especially ethylene glycol, or condensation products of terephthalic acid and 1,4-bis(hydroxymethyl)cyclohexane, for example polyethylene terephthalate (PET), polyethylene naphthalene-2,6-dicarboxylate (PEN) or polybutylene terephthalate (PBTP); also polycarbonates, e.g. those from α,α -dimethyl-4,4-dihydroxy-diphenylmethane and phosgene, or polymers based on polyvinyl chloride and on polyamides, e.g. polyamide-6 or polyamide-6,6.

The pyridone azo dyes according to the invention impart to the mentioned materials, especially to polyester material, tinctorially strong, level colour shades having very good in-use fastness properties, especially good light fastness and high-temperature light fastness. Special mention may be made of the good migration fastness and thermomigration fastness of the dyeings obtained.

The invention relates also to a process for the production of coloured plastics or polymeric colour particles, which comprises using a combination of a pyridone azo dye of formula (1) and a UV absorber, wherein the meanings and preferred meanings given above for the pyridone azo dyes of formula (1) and the UV absorbers apply.

The invention relates also to the plastics that have been mass-coloured by the processes mentioned above.

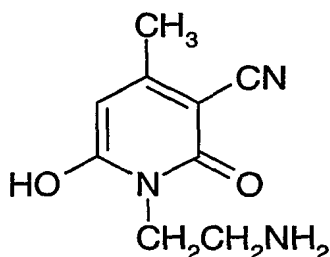
The following Examples serve to illustrate the invention. Unless otherwise indicated, the parts are parts by weight and the percentages are percentages by weight. The temperatures are given in degrees Celsius. The relationship between parts by weight and parts by volume is the same as that between grams and cubic centimetres.

Example 1:

(A) 140.0 ml of water are placed in the reactor vessel and cooled to 0-5°C. In the course of 30 minutes, 405.2 ml of ethylenediamine and then 215.4 ml of ethyl cyanoacetate are then added dropwise, the temperature being kept below 20°C by cooling. The reaction mixture is then stirred at 20°C for 16 hours, the excess ethylenediamine is distilled off *in vacuo* at 60°C and the mixture is stirred at 40°C for 1 hour.

253.0 ml of ethyl acetoacetate are then added dropwise, the temperature being raised to 70°C towards the end of the dropwise addition. As soon as the addition of the ethyl acetoacetate is complete, 168.0 ml of a 30% aqueous ammonia solution and then 1400.0 ml of propanol are added, and the reaction mixture is stirred for 16 hours at 70-75°C. The resulting suspension is filtered, introduced into 1500.0 ml of ethanol, stirred for 14 hours at 20°C and filtered again. The filter cake is washed with a total of 1000.0 ml of ethanol in portions and dried.

263.6 g of a compound of formula



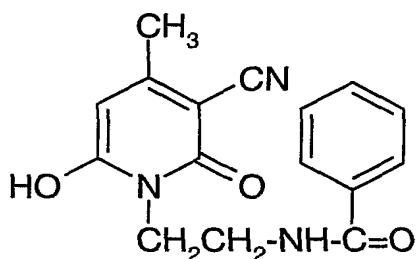
(55)

are obtained.

- 13 -

(B) 50.0 g of the compound of formula (55) are suspended in 500.0 ml of water, heated to 60°C, adjusted to pH 1.0 with 32% HCl and stirred for three hours at 60°C. A crystalline precipitate is then removed from the reaction mass by filtration, the mother liquor is adjusted to pH 9.0 with 30% aqueous NaOH, and 40.0 ml of benzoyl chloride are added. The reaction mixture is then stirred for 18 hours, the pH value being kept at 9.0, if necessary by the addition of HCl. 100.0 g of NaCl are then added, and the fully reacted reaction mass is adjusted to pH 0.5 with 32% HCl and stirred at 0°C until the product has precipitated. The precipitated reaction product is filtered off with suction and dried.

93.5 g of a product containing 62.3 g of a compound of formula



(58)

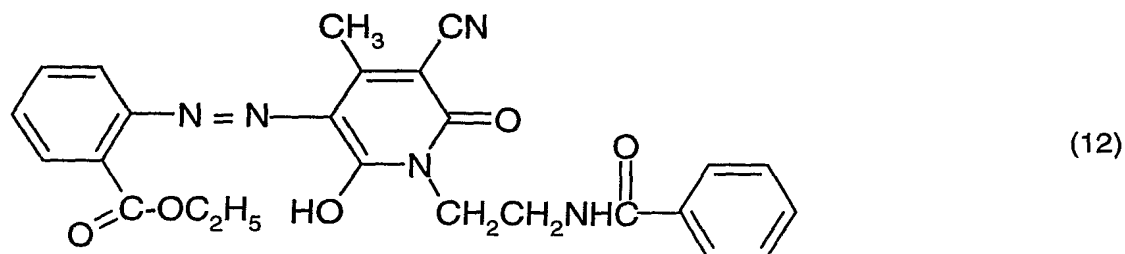
are obtained.

(C) 10.6 ml of ethyl anthranilate are placed in 110.0 ml of 98% acetic acid at from 15 to 20°C, and 22.0 g of 32% HCl are added. 17.8 ml of 4N NaNO₂ are then added dropwise to the reaction mass, and stirring is carried out for 1 hour at 10-15°C. The excess nitrite is then destroyed with sulfamic acid.

(D) 14.9 g of the compound of formula (58) prepared according to (B) are placed in 150.0 ml of water; 22.0 g of 30% aqueous NaOH are added and the mixture is heated to 50°C. 120 g of the diazo solution prepared according to (B) are then added dropwise to the resulting suspension, the temperature being kept at 15°C by the addition of about 200.0 g of ice. Once the addition is complete, the pH value is adjusted to 5.0 and the reaction mass is stirred for 16 hours.

300.0 ml of water are then added, and the fully reacted reaction mass is heated to 70°C, filtered with suction, washed with water and dried.

20.0 g of a pyridone azo dye of formula



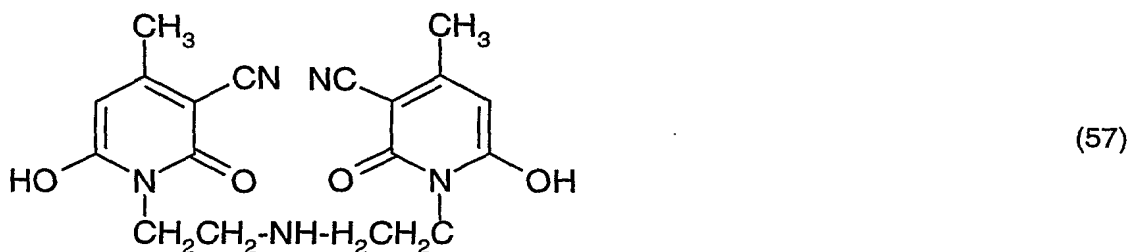
are obtained, which dyes polyester in yellow shades.

Example 2:

(A) 111.95 ml of diethylenetriamine are placed in a reaction flask and 236.95 ml of ethyl cyanoacetate are added at 20°C, the temperature rising to about 75°C. The reaction mixture is stirred for 30 minutes, and then 1000.0 ml of 94% ethanol are added and the mixture is stirred for 2 hours at 72°C (reflux). 278.3 ml of ethyl acetoacetate, 168.0 ml of a 30% aqueous ammonia solution and 3000.0 ml of 94% ethanol are then added in succession and the mixture is stirred for a further 41 hours at reflux.

The resulting suspension is filtered with suction at 75°C, then washed with a total of 500.0 ml of 94% ethanol in portions, and then 2000.0 ml of 94% ethanol are added and the mixture is stirred for 14 hours at 20°C. The suspension is then filtered with suction, the filter cake is washed with a total of 1000.0 ml of 94% ethanol in portions and dried *in vacuo*.

235.6 g of a compound of formula



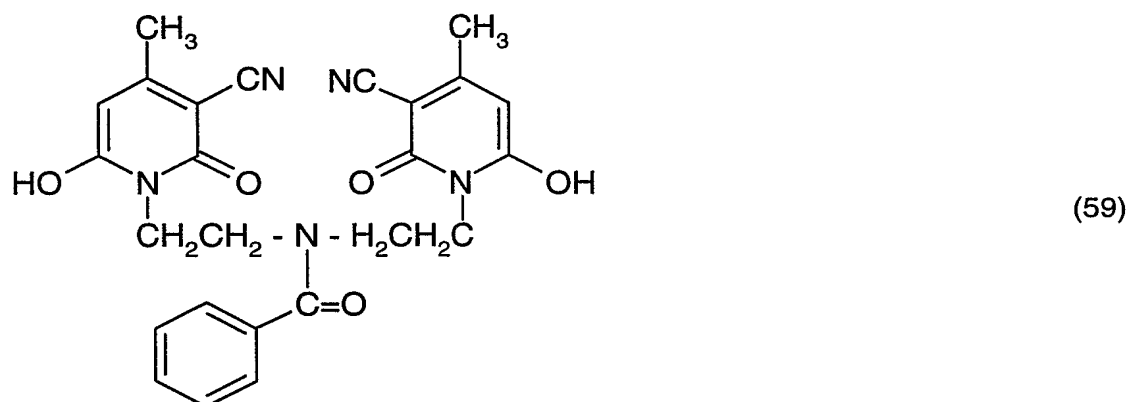
are obtained.

(B) 92.35 g of the compound of formula (57) are suspended in 1000.0 ml of water, and the suspension is heated to 60°C, adjusted to pH 1.0 with 32% HCl and stirred for three hours at 60°C. A crystalline precipitate is then removed from the reaction mass by filtration, the mother liquor is adjusted to pH 9.0 with 30% aqueous NaOH, and 40.0 ml of benzoyl chloride are added. The reaction mixture is then stirred for 18 hours, the pH value being maintained at 9.0, if necessary by the addition of HCl.

- 15 -

200.0 g of NaCl are then added and the fully reacted reaction mass is adjusted to pH 0.5 with 32% HCl and stirred at 0°C until the product has precipitated. The precipitated reaction product is filtered off with suction and dried.

90.0 g of a compound of formula



are obtained.

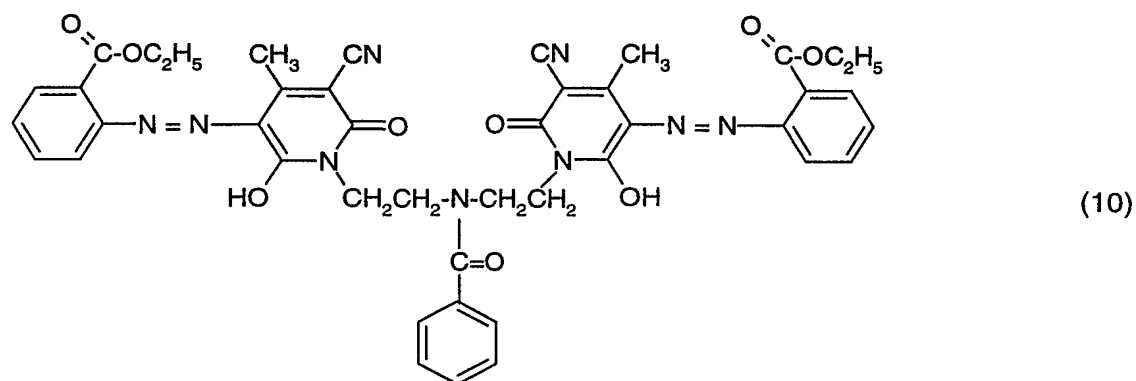
(C) 1.65 g of ethyl anthranilate are placed in 10.0 ml of glacial acetic acid at from 15 to 30°C, 0.6 ml of 96% sulfuric acid is added and the mixture is stirred for 30 minutes. 1.85 ml of 40% nitrosylsulfuric acid are then added dropwise over the course of 10 minutes to the reaction mass, and the mixture is stirred at 17-20°C for 1 hour.

(D) 100.0 ml of dimethylformamide (DMF) are taken as starting material and, with stirring, 2.4 g of the compound of formula (59) and 10.0 ml of ice water are added. Then, in the course of 30 minutes, at a temperature of 5-10°C there are added dropwise the diazo solution prepared under (C) and, at the same time, in order to maintain the pH value at 3-4, 22.0 ml of a 10% aqueous NaOH solution.

The reaction mixture is stirred for 4 hours at 0-5°C, then adjusted to pH 4.6 and stirred for a further 17 hours at 20°C. The resulting suspension is filtered with suction, washed in succession with 25.0 ml of 80% DMF, ethanol and water until pH > 6 and dried.

3.3 g of a pyridone azo dye of formula

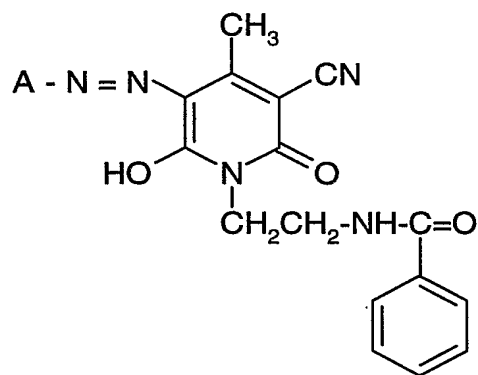
- 16 -



are obtained,
which dyes polyester in yellow shades.

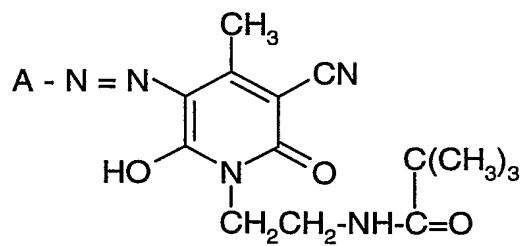
Examples 3-185: Analogously to the processes described in Examples 1 and 2, it is also possible to prepare the following dyes listed in Tables 1 to 16, which likewise dye polyester in yellow shades:

Table 1



A	A

Table 2



A	A

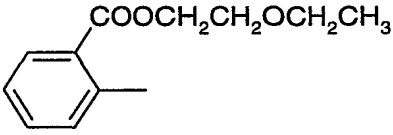
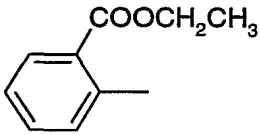
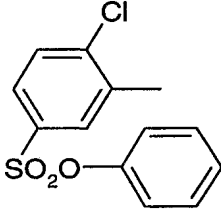
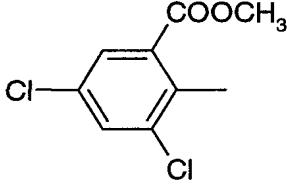
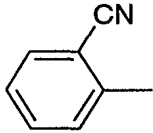
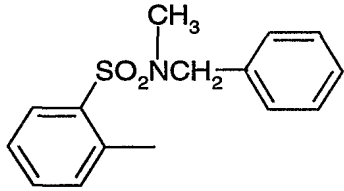
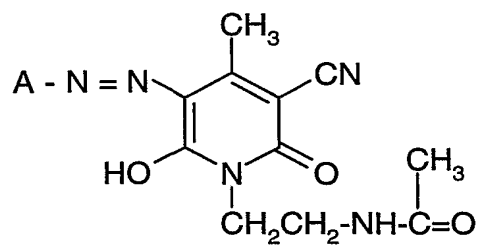
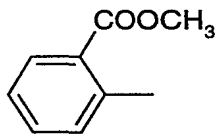
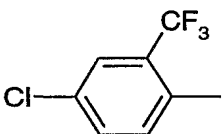
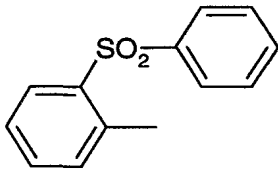
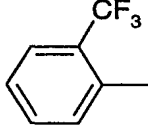
	
	
	

Table 3



A	A
	
	

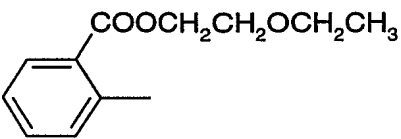
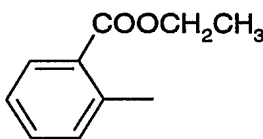
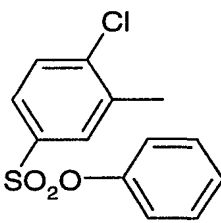
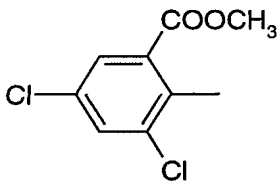
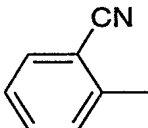
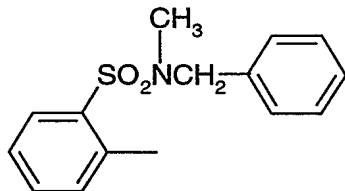
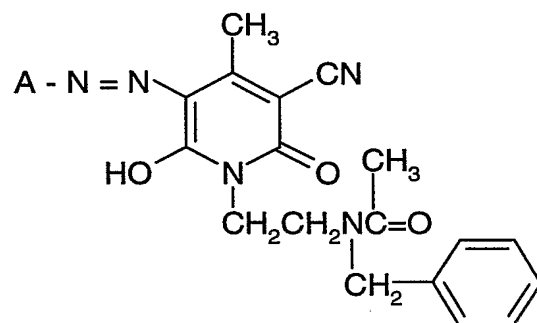
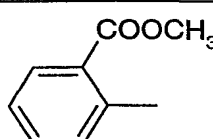
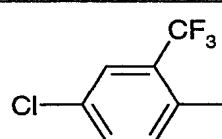
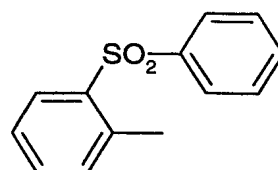
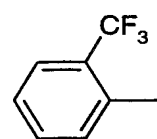
	
	
	

Table 4



A	A
	
	

- 20 -

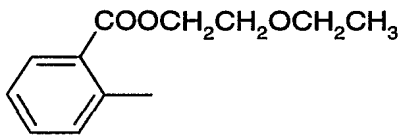
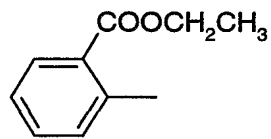
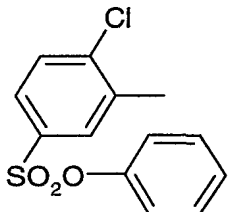
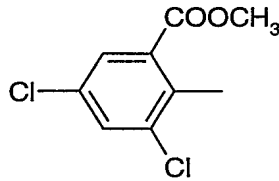
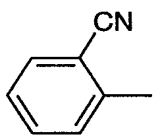
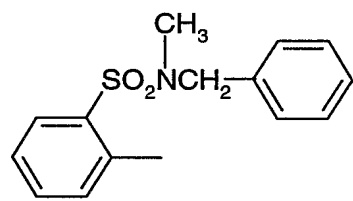
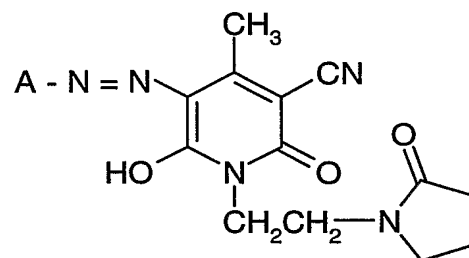
	
	
	

Table 5



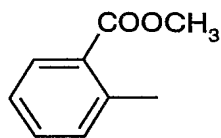
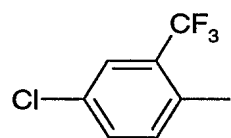
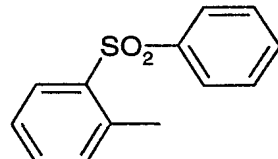
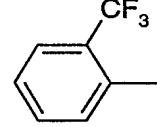
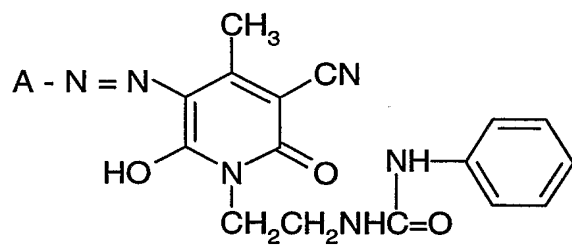
A	A
	
	

Table 6



A	A

- 22 -

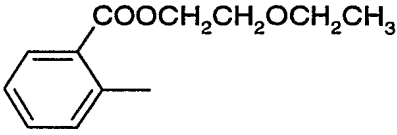
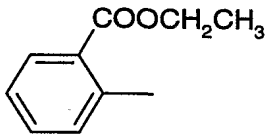
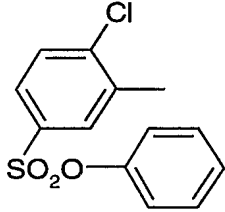
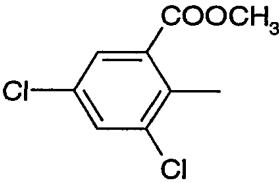
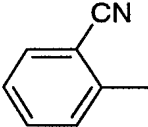

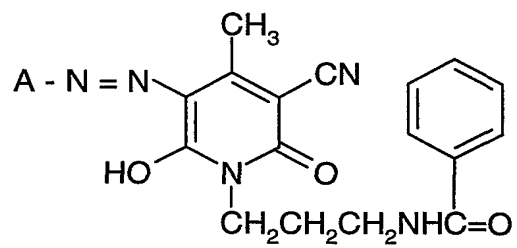
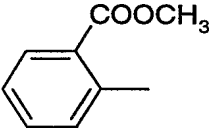
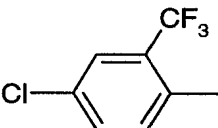
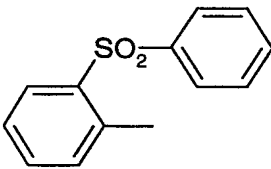
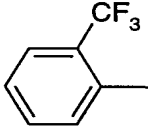
	
	
	

Table 7



A	A
	
	

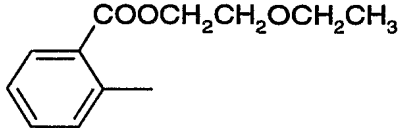
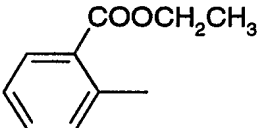
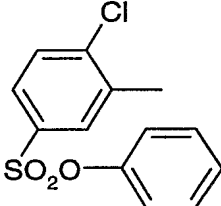
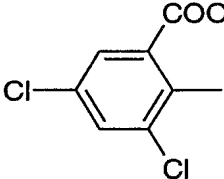
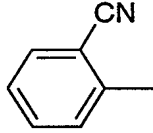

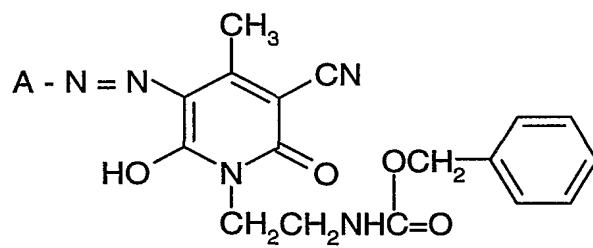
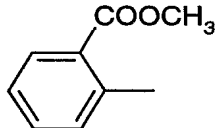
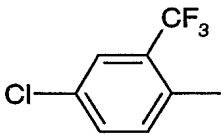
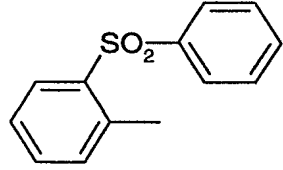
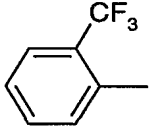
	
	
	

Table 8



A	A
	
	

- 24 -

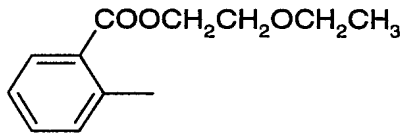
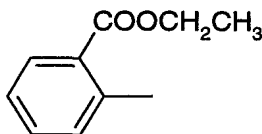
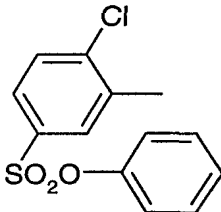
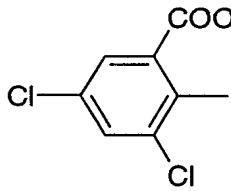
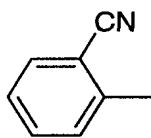
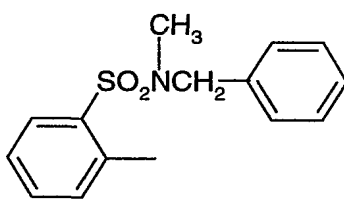
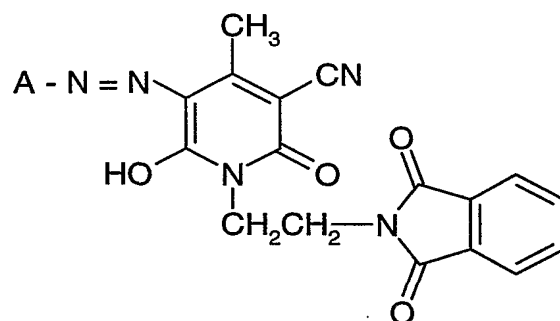
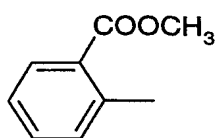
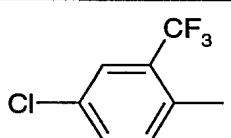
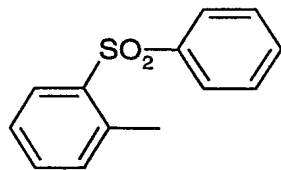
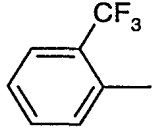
	
	
	

Table 9



A	A
	
	

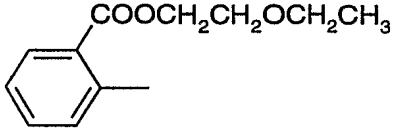
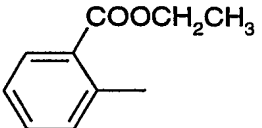
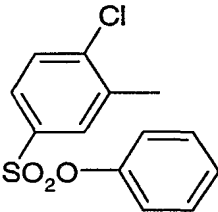
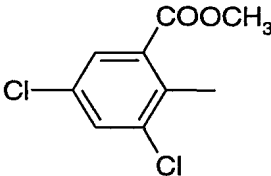
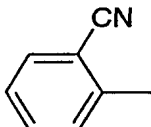
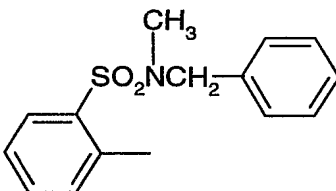
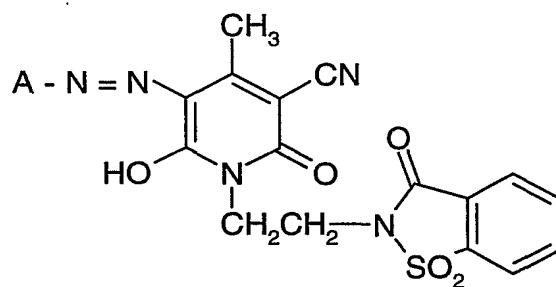
	
	
	

Table 10



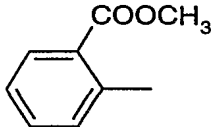
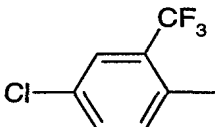
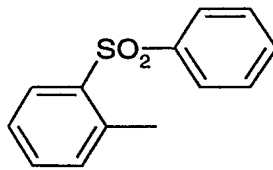
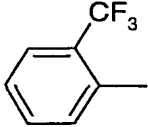
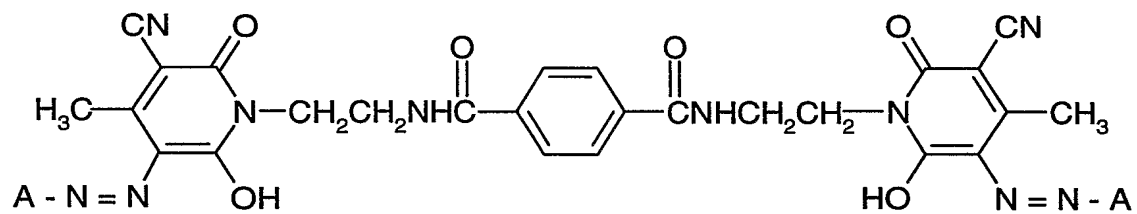
A	A
	
	

Table 11



A	A

- 27 -

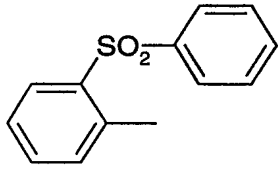
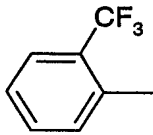
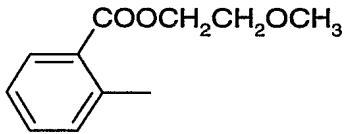
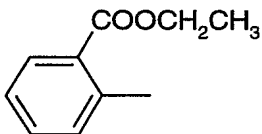
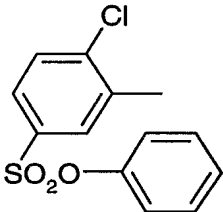
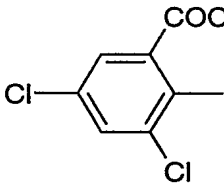
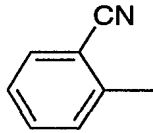
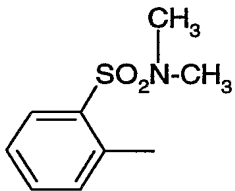
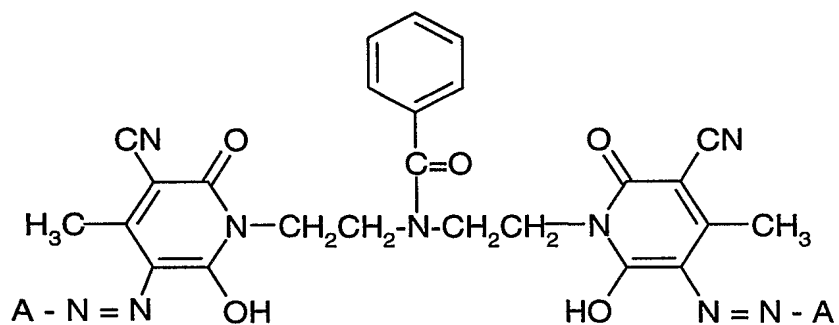
	
	
	
	

Table 12



A	A

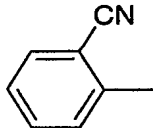
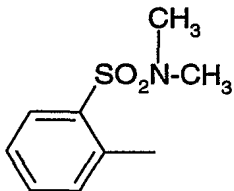
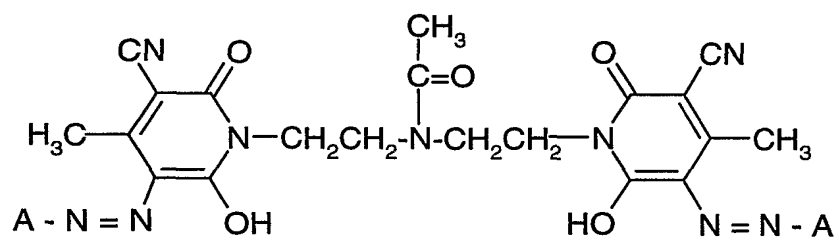
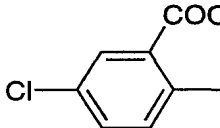
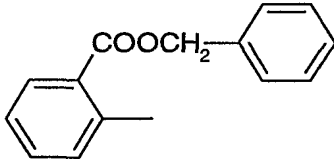
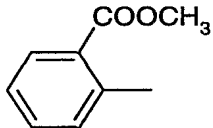
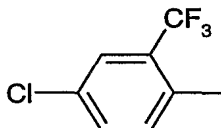
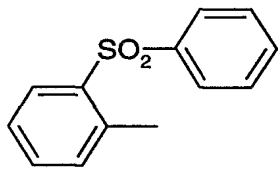

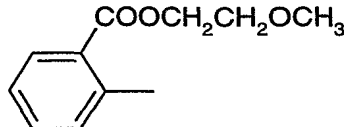
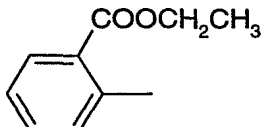
	
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Table 13



A	A
	
	
	
	

- 30 -

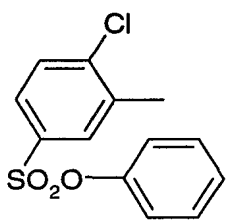
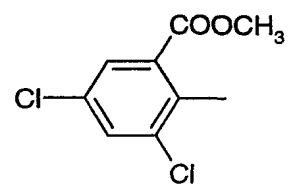
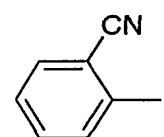
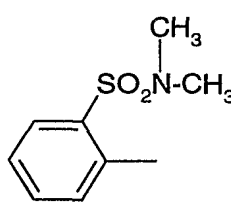
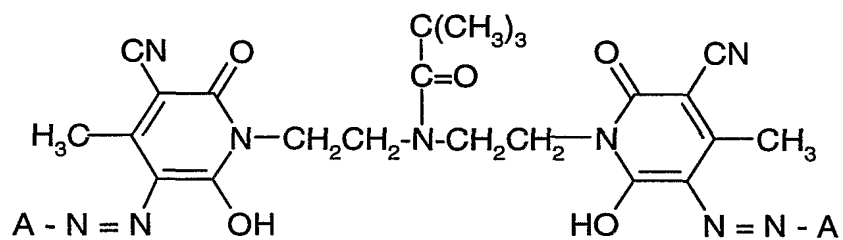
	
	

Table 14



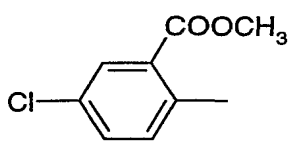
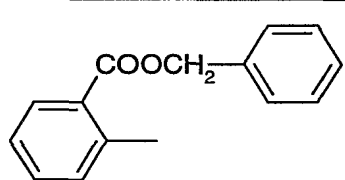
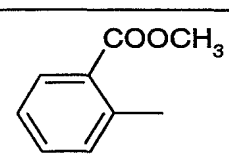
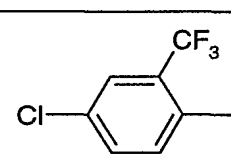
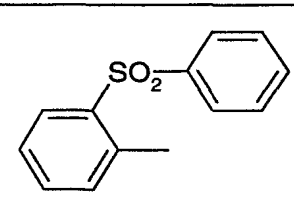
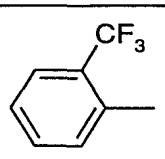
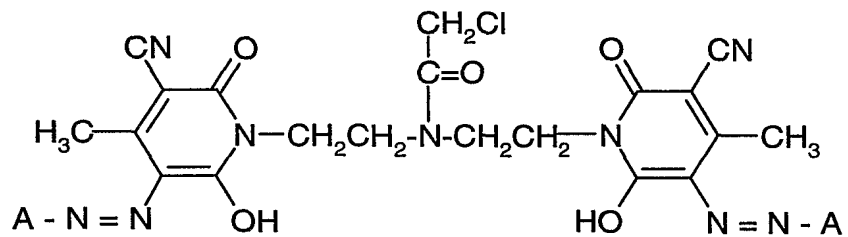
A	A
	
	
	

Table 15



A	A

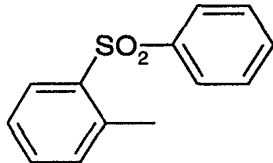
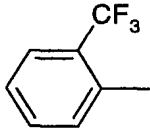
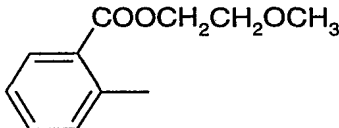
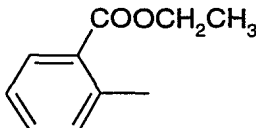
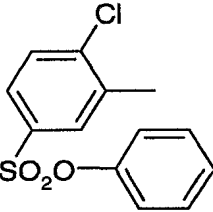
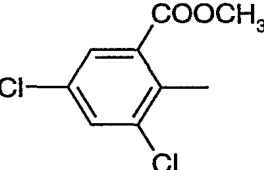
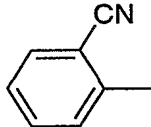
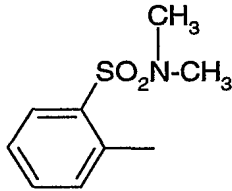
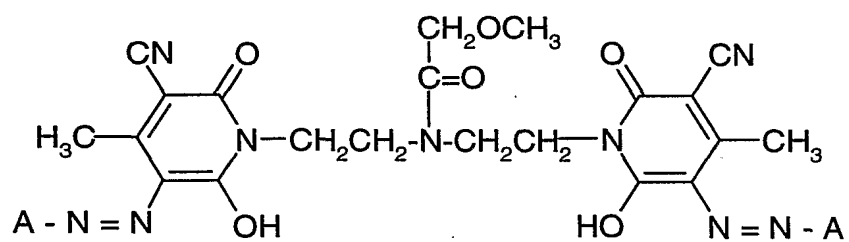
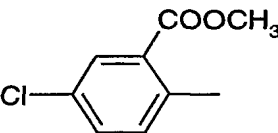
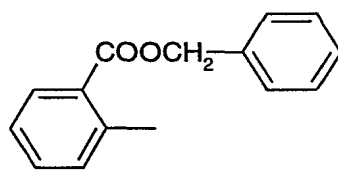
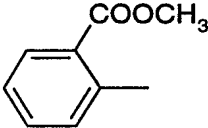
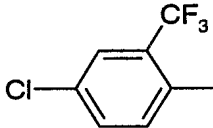
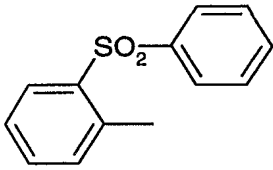
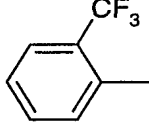
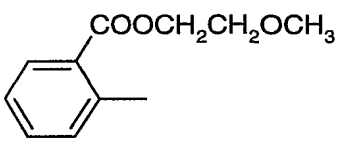
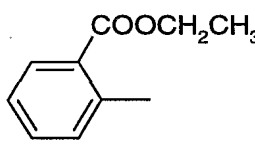
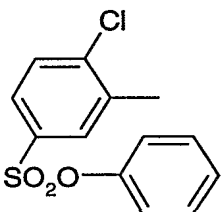
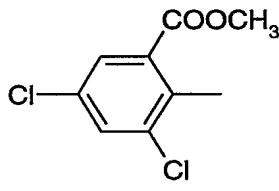
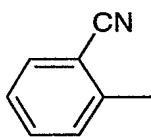
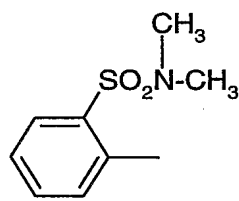
	
	
	
	

Table 16



A	A
	

Dyeing Example 1:

1200.00 g of polyester granules (PET Arnite D04-300, DSM) are pre-dried for 4 hours at 130°C and then mixed homogeneously with

0.24 g of the pyridone azo dye of formula (14)

in a "roller rack" mixing apparatus for 15 minutes at 60 revolutions per minute.

The homogeneous mixture is extruded in an extruder (twin screw 25 mm, from Collin, D-85560 Ebersberg) with 6 heating zones at a maximum temperature of 275°C, cooled with water, granulated in a granulator (Turb Etuve TE 25, from MAPAG AG, CH-3001 Bern) and then dried at 130°C for 4 hours.

The resulting yellow-coloured polyester granules have good allround fastness properties, especially very good light fastness and high-temperature light fastness properties.

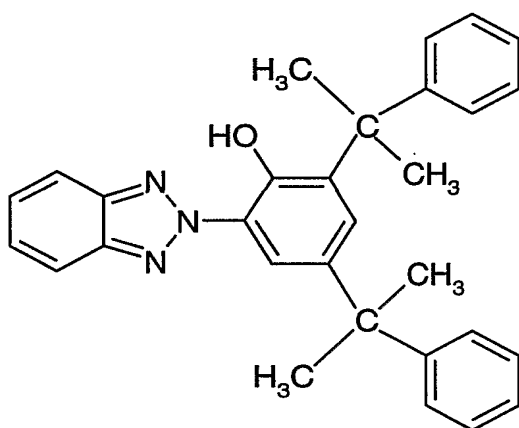
Dyeing Example 2:

1200.00 g of polyester granules (PET Arnite D04-300, DSM) are pre-dried for 4 hours at 130°C and then mixed homogeneously with

0.60 g of the pyridone azo dye of formula (14)

and

3.60 g of a UV absorber of formula



(63)

in a “roller rack” mixing apparatus for 15 minutes at 60 revolutions per minute.

The homogeneous mixture is extruded in an extruder (twin screw 25 mm, from Collin, D-85560 Ebersberg) with 6 heating zones at a maximum temperature of 275°C, cooled with water, granulated in a granulator (Turb Etuve TE 25 from MAPAG AG, CH-3001 Bern) and then dried at 130°C for 4 hours.

The resulting yellow-coloured polyester granules have good allround fastness properties, especially very good light fastness and high-temperature light fastness properties.

What is claimed is:

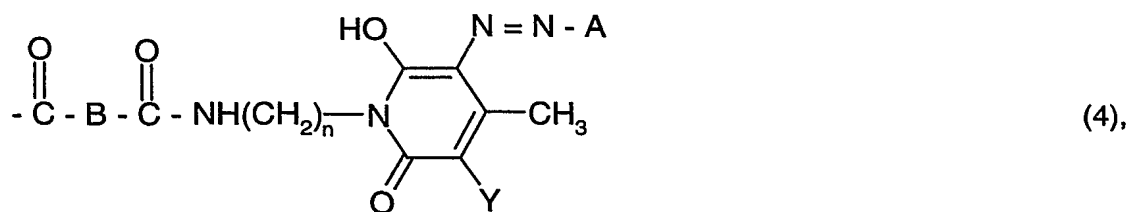
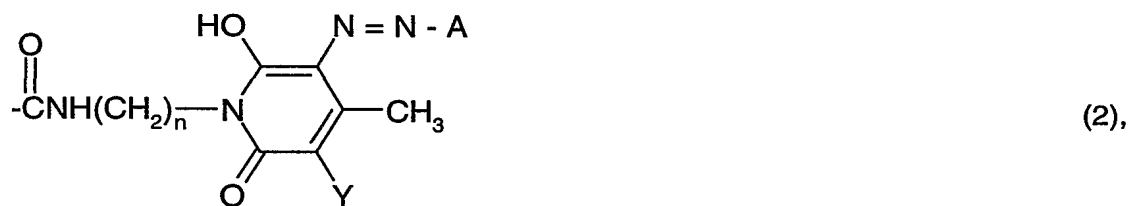
1. A pyridone azo dye of formula

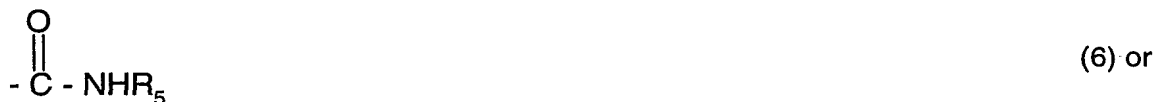


wherein

A is the radical of a diazo component of the benzene, naphthalene, diphenyl, azobenzene, thiophene, benzothiazole, benzoisothiazole, thiadiazole, indazole, benzotriazole, pyrazole, anthraquinone, naphtholic acid imide, chromone, phthalimide or diphenylene oxide series, R₁ is hydrogen, unsubstituted or hydroxy- or phenyl-substituted C₁-C₆alkyl, it being possible for the alkyl chain to be interrupted from C₃ upwards by one or more oxygen atoms, or has the meanings of R₂,

R₂ is a radical of formula





wherein B is a bridging member, R_4 is alkyl or aryl, R_5 and R_6 are each independently of the other alkyl, aryl or heteroaryl and A is as defined for formula (1), or

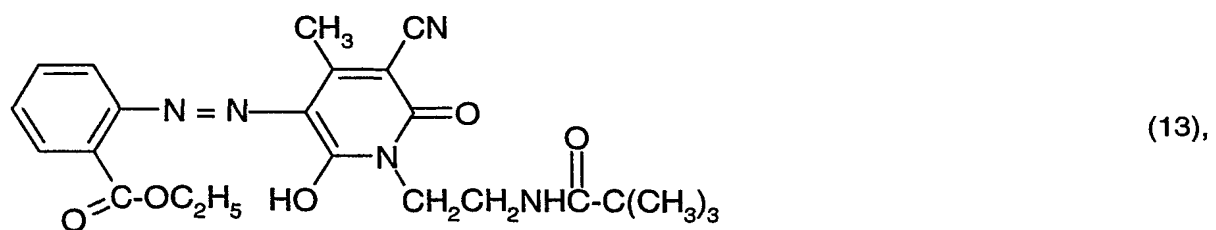
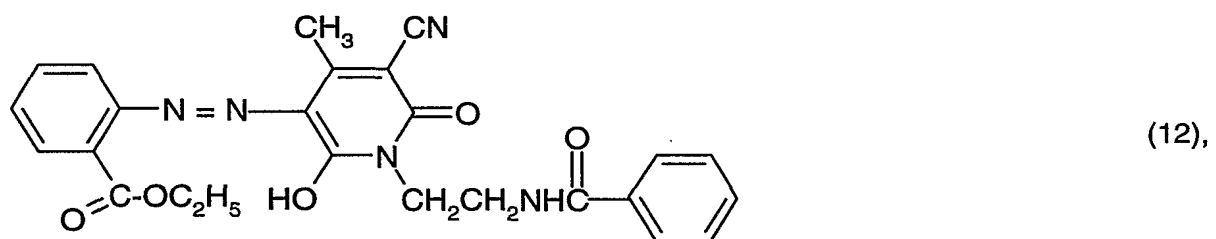
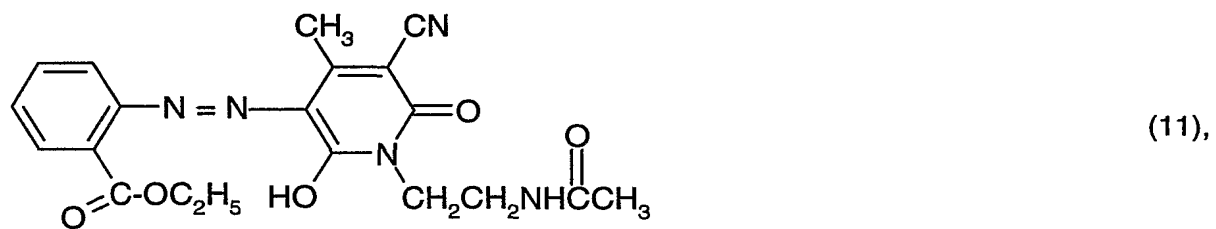
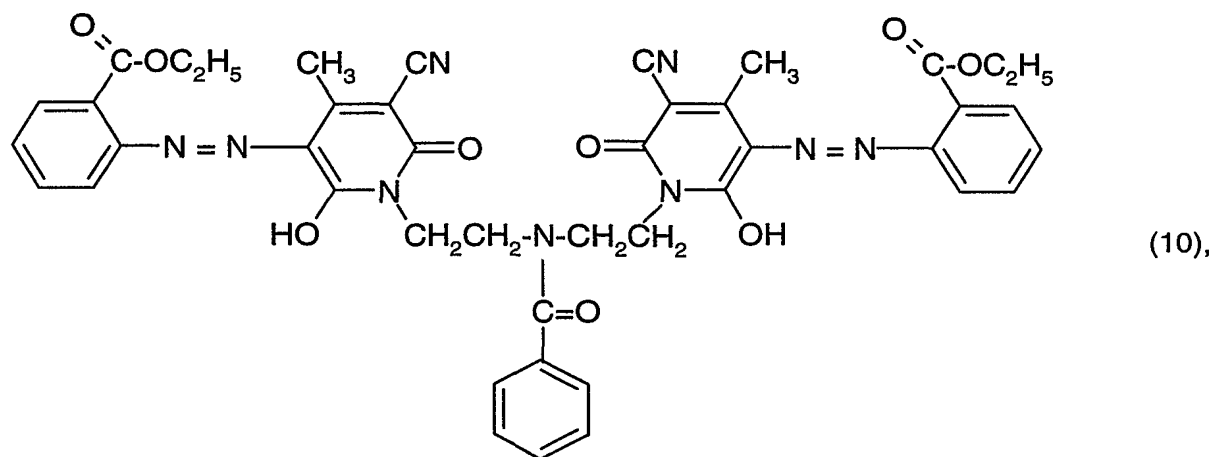
R_1 and R_2 together with the nitrogen atom in $-\text{NR}_1\text{R}_2$ form a heterocyclic ring, Y is cyano, $-\text{CONH}_2$ or $-\text{CH}_2\text{SO}_3\text{H}$, and n is an integer from 2 to 6.

2. A pyridone azo dye according to claim 1, wherein A is a radical of formula

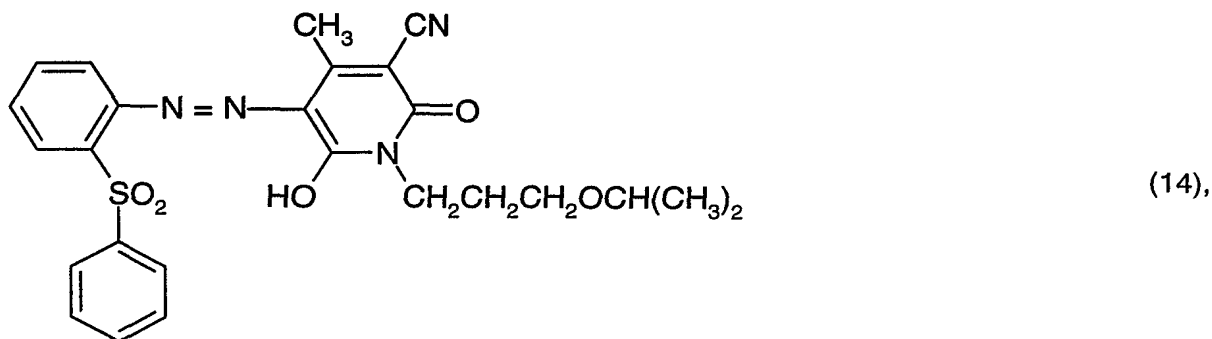


wherein R_7 is hydrogen or halogen, R_8 is hydrogen, halogen, cyano, $-\text{CF}_3$, $-\text{COOR}_{11}$ wherein R_{11} is C_1 - C_4 alkyl and the alkyl chain can be interrupted by oxygen, or is benzyl or $-\text{SO}_2\text{R}_{12}$ wherein R_{12} is $-\text{NR}_{13}\text{R}_{14}$ or phenyl and R_{13} is hydrogen or C_1 - C_4 alkyl and R_{14} is C_1 - C_4 alkyl or benzyl, R_9 is hydrogen or halogen, and R_{10} is hydrogen or a radical $-\text{SO}_2-\text{O}-\text{C}_6\text{H}_5$.

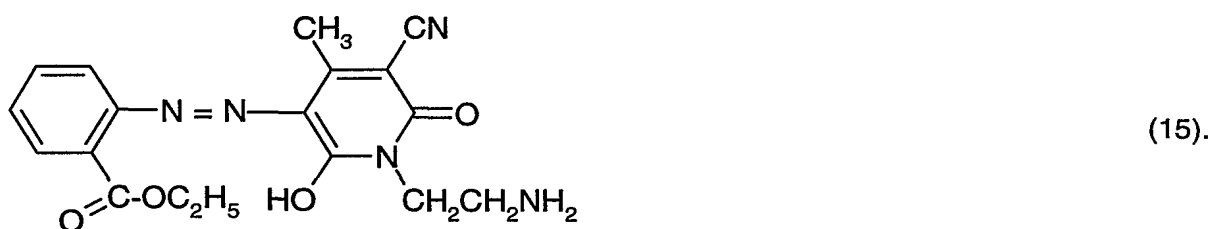
3. A pyridone azo dye according to claim 1 of formula



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or



4. A process for the preparation of a pyridone azo dye of formula (1) according to claim 1, in which process a compound of formula

A - NH₂ (50)

is diazotised in accordance with a customary procedure and then coupled to a coupling component of formula



A, R₁, R₂, Y and n being as defined for formula (1).

5. A process for the production of coloured plastics or polymeric colour particles, which comprises incorporating one or more pyridone azo dyes of formula (1) into those materials.

6. A process for the production of coloured plastics or polymeric colour particles, which comprises using a combination of a pyridone azo dye of formula (1) according to claim 1 and a UV absorber.
7. Use of a pyridone azo dye of formula (1) according to claim 1 in the production of coloured plastics or polymeric colour particles.
8. Plastics or polymeric colour particles coloured according to either claim 5 or claim 6.

INTERNATIONAL SEARCH REPORT

International Application No
PC/EP 02/02150

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09B29/36 D06P1/00 C07D213/85

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09B D06P C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, EPO-Internal, WPI Data, PAJ, BEILSTEIN Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 1 296 857 A (CIBA-GEIGY AG) 22 November 1972 (1972-11-22) *page 30, No.20; page 106, No. 43 and 44; * page 4, line 12 - line 20; claims ---	1-8
A	EP 0 763 576 A (CANON KK) 19 March 1997 (1997-03-19) claim 1 ---	1-8
A	GB 1 361 250 A (CIBA GEIGY AG) 24 July 1974 (1974-07-24) page 3, line 10; example 5 -----	1-8

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

7 May 2002

Date of mailing of the international search report

23. 07. 02

Name and mailing address of the ISA

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Authorized officer

Härtinger, S

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP 02/02150

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1 (part) - 8 (part)

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1(part)-8(part)

pyridone dyes wherein R2 is a radical of formula (2) or (4)

2. Claims: 1(part)-8(part)

pyridone dyes wherein R2 is a radical of formula (3)

3. Claims: 1(part)-8(part)

pyridone dyes wherein R2 is a radical of formula (5), (6) or
(7)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PC/EP 02/02150

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
GB 1296857	A	22-11-1972	CH 552661 A	15-08-1974
			BE 741507 A	11-05-1970
			CA 946377 A1	30-04-1974
			DE 1956142 A1	11-06-1970
			ES 373401 A1	16-01-1972
			FR 2023044 A5	07-08-1970
			JP 54032804 B	17-10-1979
			NL 6916969 A	14-05-1970
			RO 62496 A1	15-09-1978
			SE 366767 B	06-05-1974
			SU 415886 A3	15-02-1974
EP 0763576	A	19-03-1997	EP 0763576 A2	19-03-1997
			JP 9137106 A	27-05-1997
			US 5728201 A	17-03-1998
GB 1361250	A	24-07-1974	CH 599968 A5	15-06-1978
			CH 596274 A5	15-03-1978
			CH 574477 A5	15-04-1976
			AT 323162 B	25-06-1975
			AT 320099 B	27-01-1975
			AU 470322 B	11-03-1976
			AU 3688571 A	21-06-1973
			AU 3705871 A	21-06-1973
			BE 777062 A1	21-06-1972
			BE 777063 A1	21-06-1972
			CA 967574 A1	13-05-1975
			CA 972353 A1	05-08-1975
			DE 2162612 A1	13-07-1972
			DE 2162858 A1	13-07-1972
			FR 2119572 A5	04-08-1972
			FR 2119573 A5	04-08-1972
			GB 1361249 A	24-07-1974
			IT 945548 B	10-05-1973
			IT 947058 B	21-05-1973
			JP 57014779 B	26-03-1982
			NL 7117591 A	26-06-1972
			NL 7117595 A	26-06-1972
			US 4039523 A	02-08-1977
			US 3994906 A	30-11-1976
			AR 196983 A1	08-03-1974
			ES 398187 A1	16-03-1975
			ZA 7108401 A	27-09-1972